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Long term precipitation chemistry and wet deposition in a remote dry savanna site in Africa (Niger)

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Abstract. Long-term precipitation chemistry have been recorded in the rural area of Banizoumbou (Niger), representative of a semi-arid savanna ecosystem. A total of 305 rainfall samples ∼90% of the total annual rainfall) were collected from June 1994 to September 2005. From ionic chromatography, pH major inorganic and organic ions were detected. Rainwater chemistry is controlled by soil/dust emissions associated with terrigeneous elements represented by SO_4^{2-}, Ca^{2+}, Carbonates, K^+ and Mg^{2+}. It is found that calcium and carbonates represent ∼40% of the total ionic charge. The second highest contribution is nitrogenous, with annual Volume Weighed Mean (VWM) for NO_3^- and NH_4^+ concentrations of 11.6 and 18.1 μeq.l^{-1}, respectively. This is the signature of ammonia sources from animals and NO_x emissions from savannas soil-particles rain-induced. The mean annual NH_3 and NO_2 air concentration are of 6 ppbv and 2.6 ppbv, respectively. The annual VWM precipitation concentration of sodium and chloride are both of 8.7 μeq.l^{-1} which reflects the marine signature of monsoonal and humid air masses. The median pH value is of 6.05. Acidity is neutralized by mineral dust, mainly carbonates, and/or dissolved gases such NH_3. High level of organic acidity with 8μeq.l^{-1} and 5.2 μeq.l^{-1} of formate and acetate were also found. The analysis of monthly Black Carbon emissions and Fraction of Absorbed Photosynthetically Active Radiation (FAPAR) values show that both biogenic emission from vegetation and biomass burning could explain the rainfall organic acidity content. The interannual variability of the VWM concentrations around the mean (1994–2005) is between ±5% and ±30% and mainly due to variations of sources strength and rainfall spatio-temporal distribution. From 1994 to 2005, the total mean wet deposition flux in the Sahelian region is of 60.1 mmol.m^{-2}.yr^{-1} ±25%. Finally, Banizoumbou measurements are compared to other long-term measurements of precipitation chemistry in the wet savanna of Lamto (Côte d'Ivoire) and in the forested zone of Zoétélé (Cameroon). The total chemical loading presents a maximum in the dry savanna and a minimum in the forest (from 143.7, 100.2 to 86.6 μeq.l^{-1}), associated with the gradient of terrigeneous sources. The wet deposition fluxes present an opposite trend, with 60.0 mmol.m^{-2}.yr^{-1} in Banizoumbou, 108.6 mmol.m^{-2}.yr^{-1} in Lamto and 162.9 mmol.m^{-2}.yr^{-1} in Zoétélé, controlled by rainfall gradient along the ecosystems transect.

1 Introduction

Atmosphere-biosphere interactions are important to understanding the biogeochemical cycles and chemical atmospheric composition. Wet- and dry- deposition of chemical species onto the earth's surface play a key role in controlling the concentration of gases and aerosols in the troposphere. The chemical content of atmospheric deposition is the signature of several interacting physical and chemical mechanisms: i.e., emission and source amplitude; transport processes and dynamics of the atmosphere; atmospheric chemical reactions; and removal processes, among others.

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Studying deposition processes and amounts thus allow for tracing the spatio-temporal evolution of atmospheric chemistry. It is also an important way for distinguishing between natural and anthropogenic influences. In regions where natural biogeochemical cycles are perturbed by human activities, atmospheric deposition can either be important sources of toxic substances or of nutrients for the ecosystems. Knowing processes involved with chemical deposition is therefore a pre-requisite to understand and predictive the functioning of ecosystems' dynamics (Brimblecombe et al., 2007; Whelpdale et al., 1996).

The international program DEBITS (Deposition of Biogeochemically Important Trace Species) started in 1990 as part of the IGAC/IGBP (International Global Atmospheric Chemistry/ International Geosphere-Biosphere Programme) "Core Project". It is to study wet- and dry- atmospheric deposition in tropical regions (Lacaux et al., 2003; IGAC, 2003). The DEBITS network includes fifty measuring stations well distributed within the tropical belt. DEBITS activities have been positively reviewed and are thus continuing within the new IGAC structure or DEBITS II (Pienaar et al., 2005; Bates et al., 2006). For tropical Africa, the IDAF (*I*GAC/*D*EBITS/*AF*RICA) Project started in 1994. Since IDAF has been recognized by INSU (Institut National des Sciences de l'Univers, in French) and the CNRS (Centre National de la Recherche Scientifique, in French) as a part of the Environmental Research Observatory (ORE, in French) network. ORE/IDAF has the mission of establishing a long-term measuring network to study the atmospheric composition and wet- and dry- atmospheric processes and fluxes. The IDAF program is associated with the African Monsoon Mutidisciplinary Analyses/Long Observation Program (AMMA/LOP, Lebel et al., 2007) over West/Central Africa and with the South African Climate Change Air Pollution-PICS (SACCLAP) Program. The main objectives of IDAF were to measure wet- and dry- deposition fluxes and identify the relative contribution of natural and anthropogenic source. The IDAF project implemented 8 monitoring sites covering three types of ecosystems over West and Central Africa: dry savanna (Niger, Mali, South Africa), wet savanna (Côte d'Ivoire and Benin) and equatorial forest (Cameroon). Data from the measuring site at Banizoumbou (Niger), which represents the African dry-savanna ecosystem, is analyzed here.

It is important to notice that multidisciplinary research has been recently receiving considerable attention, mainly within arid and semi-arid environment where ecosystems are characterized by low, discrete rainfall, high temperature, periodic droughts with little vegetation cover (Estell et al., 2006). The transition from the dry season to the wet season is controlled by the monsoon regime. In the Sahel severe drought-periods have been observed during the 1970's and 1980's with large meso-scale variability (Lebel et al., 1992, 2003; Le Barbé and al., 2002; Messager and al., 2004, Balme et al., 2006) and specific hydrological processes (Goutorbe et al., 1994). Moreover emissions in the troposphere are increasing as a response to environmental rapid changes (Jaegle et al., 2005; Otter et al., 2005).

Sahelian vegetation density depends also upon monsoonal rainfall variability (Jarlan et al., 2005; Martiny et al., 2005). At the same time the population growth (with a 2-fold increase in the last 40 years) and intense land-use enhance desertification processes (Rayanaut, 2001) which partly explains the intensification of dust emissions and increase of dust transport over the tropical north-Atlantic (Moulin and Chiapello, 2006).

Rainwater chemistry in arid and semi-arid environments have been reported in India (Norman et al., 2001; Satsangi et al., 1998). These studies analyze the precipitation chemistry for one rainy season only. In Central and Western Europe (Puxbaum et al., 2002), in North America (Likens et al., 2001), in Central Austria (Puxbaum et al., 2002), in Brazil (Fornero et al., 2006), and in Israel (Mamane and Gottlieb, 1995; Herut et al., 2000) long-term precipitation chemistry trends have also been performed. All these studies are related to urban areas and trends are associated with anthropogenic sources.

Results from other African ecosystems have been recently published (Yoboué et al., 2005; Sigha et al., 2003; Mphepya 2004, and 2005). Results on rainwater chemistry measured at the Banizoumbou site during the 1996 rainy season only have been published (Modi et al., 1996; Galy-Lacaux and Modi, 1998; Galy-Lacaux et al., 2001).

In this paper, it is proposed for the first time to study long-term precipitation chemistry (1994–2005) along with wet-deposition measurements at the dry-savanna site of Banizoumbou (Niger). It is an attempt at characterizing wet-deposition in the Sahelian region with the objectives to establishing linkages between seasonal cycle and inter-annual variability. After knowing the mean composition of wet- deposition fluxes, it becomes possible to investigate the relative influence of the natural versus anthropogenic sources. Amount of atmospheric particles, trace gases along with the variability of annual rainfall should allow for a better understanding of rainfall chemical content and associated wet- deposition fluxes. Results here can be compare to that from other IDAF sites representative of African wet- savanna and equatorial forested ecosystems. This paper contributes to the interdisciplinary research needed in arid and semi-arid environment.

2 Experimental site

In Fig. 1 the location of the 8 IDAF sites operating in 2006 are displayed and superimposed with the vegetation map of Africa (Mayaux et al., 2004). Banizoumbou (13.33° N, 2.41° E) is located in a rural and agro-pastoral area of Niger, approximately 60 km eastward of Niamey. The site belongs to the degree-square

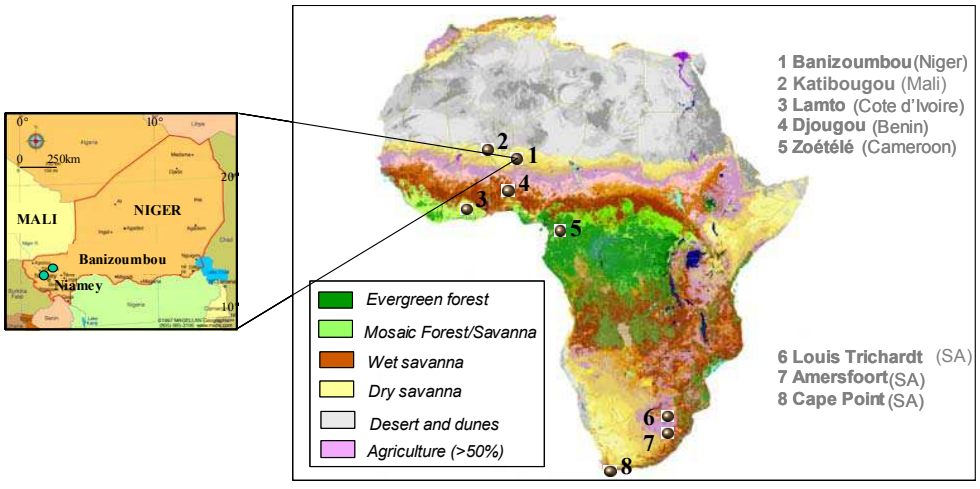


Fig. 1. Vegetation and localization map of the 8 measurement stations of the IDAF network Zoom on the map of Niger with location of the IDAF site of Banizoumbou.

around Niamey (13–14° N; 2–3° E), part of the survey network of the HAPEX-Sahel experiment in 1992 (Goutorbe and al., 1994). The Banizoumbou site belongs also to other measuring programs such AERONET/Photon (National Observatory for Aerosol, http://loaphotons.univ-lille1.fr/photons/), CATCH (Couplage de l'Atmosphère Tropicale et du Cycle Hydrologique, http://www.lthe.hmg.inpg.fr/catch/), ROSELT (Réseaux d'Observatoires et de Surveillance Ecologique à Long Terme, http://www.oss-online.org/). In 1994, the site was included in the IDAF network. In 2004, the site has been naturally included in the AMMA. The site is equipped to perform long-term monitoring of wet- and dry- atmospheric deposition. It includes the measurements of each rainfall event (see Sect. 3) with analyses of chemical composition of NO_2, NH_3, HNO_3, O_3, and SO_2. The climate of the studied region is typically Sahelian with a dry season from October to May and a wet season from June to September. These seasons are linked to the shift of the Inter Tropical Convergence Zone (ITCZ) which divides hot and dry continental air coming from the Sahara desert (harmattan northeasterlies) and cooler and humid maritime air masses from the equatorial Atlantic Ocean (summer monsoon southwesterlies). In January, the ITCZ is located ∼5° N, corresponding to the dry season in the Sahel. In August, the ITCZ reaches ∼23° N, at the heart of the rainy season in West Africa. The annual rainfall amount varies from 800 mm to the south, to 200 mm in the north, with a meridional gradient of 1 mm km^{-1} (Lebel et al., 1992, 2003).

The Sahelian rainfall is characterized both by strong interannual variabilities and by periods of droughts (1968–1997). At the Banizoumbou site rainfall variability is representative to that of the entire Sahel from 1950 to 2002 (20° W–20° E; 10° N–20° N) (Balme et al, 2006). Here eleven years of rain chemistry at the Banizoumbou site are analyzed (1994–2005). The mean annual rainfall at Banizoumbou is 495.1 mm (Table 1). In the time-series, rainfall amount larger than the mean are for 1994 (689 mm, or +38%) and 1998 (699 mm, or +41%). Also, rainfall deficit of more than 20% are registered during the 2000-2005 period with one exception during 2003.

3 Measuring procedure and chemical analysis

3.1 Rain sampling

Event sampling was carried out at the monitoring station using an automatic precipitation samplers, which have been designed for the IDAF network. These operate according as follows:

– rainwater is collected using a single-use polyethylene bag, avoiding aerosol deposit before the onset of the rain. A precipitation sensor automatically controls the aperture of the sampler cover, which hermetically closes the polyethylene bag. The area of rain collection is 225 cm^2.

– after each rainfall event, 50 cm^3 of the collected water are distributed in 50 ml essay-tubes (Greiner-type). Preserving rainwater from contamination is derived from the Gillett and Ayers (1991) technique. Samples are refrigerated (4°C) or frozen (−18°C) and stored with 15 mg of thymol biocide. In parallel, references essay-tubes filled with 15 mg of thymol and de-ionized water are analyzed by Ionic Chromatography (IC) for blank values.

Table 1. Rainwater collection in Banizoumbou (1994–2005): Annual rainfall (H) in mm, the Inter-annual variability of precipitation at Banizoumbou in % (X%), calculated from the deviation of annual precipitation to the mean annual rainfall for the period 1994–2005 (495.1 mm), collected rainfall depth (Hc) in mm and Efficiency Collection (EC) in %.

Year	H	H_C	EC
1994	689.1 (+39%)	640.2	93
1995	455.5 (−8%)	–	–
1996	503.5 (+2%)	384.4	76
1997	489.0 (−1%)	418.5	86
1998	699.2 (+41%)	657.2	94
1999	533 (+8%)	525.9	99
2000	407.2 (−18%	385.5	95
2001	401.8 (−19%)	350.1	87
2002	418.2 (−16%)	384.0	92
2003	518.8 (+5%)	476.0	92
2004	420.5 (−15%)	355.7	85
2005	404.9 (−18%)	372.0	92
Total	5941.1	4949.5	90
Mean	495.1	450.0	

From June 1994 to September 2005 (excluding 1995), 305 rainy events, representing a total rainfall amount of 4949.5 mm were collected. The total rainfall amount during the eleven years is 5485.6 mm (Table 1). The efficiency of collection (EC) is calculated for each studied year and is between 76% and 99%. The mean EC equals to 90% corroborates the good representativity of the dataset. The annual mean rainfall amount during the period of study (1994–2005) (495.1 mm) is comparable to the annual mean collected rainfall (450 mm).

3.2 Gaseous passive samplers measurements

Measurements of monthly mean gaseous nitrogen dioxide (NO_2) and ammonia (NH_3) in the dry-savanna of Banizoumbou have been performed since 1998. Gaseous NO_2 and NH_3 were collected using passive sampling techniques. These measurements are based on the property of molecular diffusion of gases and species collection on an impregnated filter specific to each pollutant. In the IDAF project, a set of passive samplers was developed at the laboratory of "Aerologie" (Toulouse). Two separate samplers are required for NH_3 and HNO_3, since different impregnated filters are needed. For NH_3, we used 1 g of citric acid diluted in 50 ml of methanol and for HNO_3 0.5 g of NaOH diluted in 50 ml of methanol. The sorption processes for these two gases occur though the following reactions:

$$NH_3(gas) + H^+ \rightarrow NH_4^+ \quad (1)$$

$$HNO_3(gas) + OH^- \rightarrow H_2O + NO_3^- \quad (2)$$

The collecting filter inside the sampler is protected against mechanical impact (insect) and wind turbulence by a metallic thin stainless-steel mesh. In addition, a 1 μm teflon filter is used to exclude aerosol particles contamination by impaction onto the impregnated filter. Samplers were sent to- and-from the site in sealed plastic containers (following Ferm, 1991). To prevent contamination of samplers by particles, the inlet part of the sampler is replaced by a solid cap immediately after sampling (Ferm and Rodhe, 1997). On site, a passive pair of gas samplers were active for one-month periods. They were mounted under a plastic disc (attached to a pole of ∼1.5 m) to avoid direct effect of wind transport and splashing from precipitation.

The ambient gas concentration C_x collected by the passive sampler was calculated from the amount trapped on the sorbant filter (X in mol), the time of exposure (t in s), the diffusion coefficient of the gas (D_x) and geometric characteristics of the sampler. Details are found in Galy-Lacaux et al. (2001). Passive samplers have been tested and validated since 1998 (Al Ourabi and Lacaux, 2002). Samplers are attached to a pole at 1.5 m high or more.

The limits of the passive samplers were tested by comparing with 'blank amounts' from impregnated filters. The blanks and associated standard deviations were 1.5 ppb for NH_3 and 0.15 ppb for HNO_3. The reproducibility calculated from the paired samplers gives an indication of the precision of this sampling technique. It is about 20% and 15% for HNO_3 and NH_3, respectively. Some tests have been performed to optimize the sampling period duration. In all the IDAF non perturbed rural areas, the levels of gaseous concentration (0–10 ppb) require an integration of about four weeks. In South African IDAF sites, the monthly monitoring of gases has been successfully compared to active gas measurements (Martins et al, 2007). In other different tropical and subtropical regions of Asia or India, Carmichaël et al. (2003) determine also monthly concentrations. In urban sites such Dakar (Senegal) and Bamako (Mali), the use of the IDAF passive sampler shows saturation after a two week exposition with levels of concentrations ten times higher

3.3 Chemical analysis

The composition of the rainwater samples was determined at the Aerologie Laboratory in Toulouse. Inorganic (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, NO_3^-, SO_4^{2-}), carbonates and organic ($HCOO^-$, CH_3COO^-, $C_2H_5COO^-$, $C_2O_4^{2-}$) ions are measured by ion chromatography (IC). The laboratory is equipped with a DIONEX DX500 and ICS 1000 ionic chromatograph (IC) with two automatic samplers (AS50). The determination of anions and organic acids on the DX500 used a gradient pump (GP40), with a conductivity detector (CD20), and a DIONEX Ionpac AS-11 and AG-11 as pre column. Carbonates are analysed with the DX500, using an AS1 column with ionic exclusion and an isocratic mode (100% H_2O). For cations detection, the ICS 1000 in an isocratic

Table 2. Correlation coefficients between ions in rainwater over the eleven years (1994–2005). The "Spearman" method was used with a 1% confidence level.

	H^+	Na^+	NH^+_4	K^+	Ca^{2+}	Mg^{2+}	NO^-_3	Cl^-	SO^{2-}_4	$HCOO^-$	CH_3COO^-	$C_2O^{2-}_4$
H^+	1.00											
Na^+		1.00										
NH^+_4		0.55	1.00									
K^+		0.81	0.63	1.00								
Ca^{2+}		0.52	0.62	0.51	1.00							
Mg^{2+}		0.52	0.59	0.66	0.85	1.00						
NO^-_3	0.46	0.50	0.74	0.59	0.75	0.75	1.00					
Cl^-		0.78	0.49	0.74	0.36	0.40	0.45	1.00				
SO^{2-}_4	0.31	0.62	0.61	0.46	0.83	0.72	0.74	0.44	1.00			
$HCOO^-$	0.81		0.64				0.59		0.29	1.00		
CH_3COO^-	0.57		0.72				0.67		0.50	0.71	1.00	
$C_2O^{2-}_4$	0.33	0.24	0.63	0.72	0.55	0.55	0.71	0.05	0.58	0.57	0.68	1.00

mode with CG12A and CS12A as pre-column and column, was used. The eluents were NaOH and MSA for anions and cations, respectively. Certified ionic standards were used for IC calibration. According to prior results and through inter-comparison tests organized by WMO (World Meteorological Organization, 1997), analytical precision is estimated to be 5% or better for all ions, within the uncertainties on all measured values presented here.

To improve the quality of the IDAF dataset, the WMO quality criteria were applied to all the IDAF precipitation samples. These criteria were based on the calculation of the ion difference (ID) for each sample to consider the ionic balance:

$$\text{Ion Difference } \% = 100 \times ([\text{CE} - \text{AE}]/[\text{CE} + \text{AE}]) \quad (3)$$

AE is the anion sum in μeq.l^{-1} and CE is the cation sum in μeq.l^{-1}. WMO acceptance criteria are presented in WMO report (1997). In this study, the ID criteria has been applied to all 338 samples in Banizoumbou (1994–2005). 90% of the samples within the WMO acceptance range were considered here.

The pH is measured with an ATI Orion 350 instrument with a combined electrode (ATI Orion model 9252) filled with KCl (4 M) and satured with AgCl. Two standard solutions (WTW) at pH 4.01 and 7.00 are used for its calibration. From the pH values, ion H^+ concentrations are calculated. The precision is of 0,01 pH unit.

3.4 Calculations – Annual volume-weighted mean and wet deposition at the Banizoumbou site

The annual volume-weighted mean concentrations (VWM) of ionic constituents in Banizoumbou rainwater have been calculated using:

$$\text{VMW}(\mu\,\text{eq}.l^{-1}) = \sum_{i=1}^{N} \mathbf{C}_i \mathbf{P}_i / \sum_{i=1}^{N} \mathbf{P}_i \quad (4)$$

where $\mathbf{C}_i$ is the ionic concentration for each element in μeq.l^{-1}, $\mathbf{P}_i$ the precipitation amount for each rainy event in mm, and N the total number of samples. To calculate the mean VWM concentration of each ion over the period 1994–2005, with N=305.

The annual Wet Deposition (WD) expressed in mmol.m^{-2}.yr^{-1} is calculated by multiplying the VWM concentrations by the annual rainfall amount. To calculate the mean WD over the 11 years, the mean annual rainfall from 1994 to 2005 is used, i.e., 495.1 mm. Concentrations of H^+ were calculated from the measured pH values. Correlation coefficients using the Spearman Method are presented in Table 2. These correlation coefficients between the different chemical parameters will be examined in order to determine the potential sources that influence the rainwater composition. High correlation could indicate that chemical compounds have the same origin and/or are being advected by the same air masses.

To estimate the contribution of sea salt component to the precipitation composition measured in Banizoumbou, excess concentration with respect to sea salt (X*) of sulfate, chloride, potassium, calcium and magnesium using Na^+ are calculated. Reference and ratios for seawater composition are given by Keene et al. (1986). Table 4 presents different ratios: Cl^-/Na^+, SO^{2-}_4/Na^+, K^+/Na^+, Ca^{2+}/Na^+ and Mg^{2+}/Na^+ in sea water and in rain water and give the calculation of the enrichment factors (EF) of different components with respect to Na^+

$$\text{EF} = (\text{X}/\text{Na}^+)_{\text{rain}}/(\text{X}/\text{Na}^+)\ \text{seawater} \quad (5)$$

4 Results – Precipitation chemical composition and wet deposition

From the entire database the mean annual chemical composition of rainfall and associated wet- deposition are evaluated.

Table 3. Annual Volume Weighted Mean (VMW) concentrations in μeq.l^{-1} measured at Banizoumbou during the period 1994–2005.

	1994	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	1994–2005
H^+	-	2.4	1.9	2.4	-	1.9	-	2.4	1.8	2.0	2.3	2.3
pH	-	5.62	5.72	5.62	-	5.7	-	5.62	5.70	5.70	5.60	6.05***
Na^+	8.9	7.7	6.2	6.7	8.3	11.1	12.6	9.6	8.3	11.0	9.7	8.7
K+	7.6	4.7	3.9	9.1	5.5	5.4	7.2	8.2	8.0	7.9	7.4	7.5
Ca^{2+}	23.6	28.3	34.6	27.2	24.1	25.7	36.3	26.3	23.8	31.9	23.4	27.3
Mg^{2+}	6.0	5.2	7.4	6.8	5.4	8.3	8.4	8.7	6.8	5.8	5.1	6.7
NH_4^+	20.6	12.9	16.0	16.4	18.8	14.3	15.6	19.1	16.5	20.8	20.6	18.1
NO_3^-	12.4	12.1	11.7	12.1	10.3	9.3	15.2	15.2	9.4	12.3	10.2	11.6
Cl^-	9.2	7.4	5.4	8.6	7.8	9.9	10.7	12.2	7.4	11.0	8.7	8.7
SO_4^{2-}	9.6	8.2	8.8	9.0	8.5	10.0	11.6	10.2	10.9	11.6	7.6	9.4
t carb**	27.3	23.4	21.6	24.1	23.2	26.1	40.9	26.0	37.3	23.9	28.3	28.2
HCOO	-	5.7 (5.4*)	7.8 (7.7*)	8.8 (8.7*)	-	-	-	9.3 (9.1*)	7.9 (7.8*)	8.6 (8.5*)	7.8 (7.7*)	8.1 (8.0*)
CH_3COO	-	3.8 (2.3*)	4.6 (4.2)	5.9 (5.3*)	-	-	-	6.6 (5.7*)	5.9 (5.4*)	8.2 (7.5*)	6.3 (5.7*)	5.9 (5.2*)
C_2H_5COO	-	0.3 (0.2*)	0.3 (0.3)	0.2 (0.1*)	-	-	-	1.2 (1.1*)	-	0.2 (0.2*)	0.3 (0.2*)	0.4 (0.4*)
C_2O_4	-	-	-	1.6 (1.6*)	-	-	-	2 (1.9*)	1.4 (1.4*)	2.6 (2.6*)	2.8 (2.7*)	2.0 (2.0*)

*Dissociated fraction of organic acids are noted in brackets.
*t carb is total carbonates.
**median pH

Table 4. Comparison of sea water ratios with rain water components at Banizoumbou.

	Cl^-/Na^+	SO_4^{2-}/Na^+	K^+/Na^+	Ca^{2+}/Na^+	Mg^{2+}/Na^+
Sea water ratios (Keene et al., 1986)	1.16	0.121	0.022	0.044	0.227
Ratios in rain	1.000	1.080	0.862	3.138	0.770
EF 0.9	8.9	39.2	71.3	3.4	

Results are analyzed according to the combination of physical and chemical processes, i.e., meteorological parameters and atmospheric aerosols and gases sources strength in relation with measured precipitation chemistry. Then, the interannual trends were analyzed. The latter allows to evaluate rainfall chemistry characteristics for the African dry-savanna ecosystem. The mean composition is compared to that from other IDAF sites representatives of semi-arid savannas in West and South Africa, wet-savanna and forested ecosystems.

Calculation of the annual VWM and the annual mean VWM for all the datasets are presented in Table 3. The calcium ion is the most abundant in Banizoumbou rainwater samples (27.3 μeq.l^{-1}). The second most dominant ion is the NH_4^+ (18.1 μeq.l^{-1}), followed in decreasing order by NO_3^-, SO_4^{2-}, Na^+, Cl^-, formate, K^+, Mg^{2+}, acetate, oxalate and propionate.

4.1 Marine and Terrigenous contributions

The annual VWM concentration of sodium and chloride are equal to the same value 8.7 μeq.l^{-1} (Table 3). A linear relationship between Na^+ and Cl^- (r=0.78) (Table 2) and a mean annual ratio of 1.00 close to the seawater ratio (1.16) is observed (Keene et al., 1986). Back trajectories have been calculated with the Hysplit model (http://www.arl.noaa.gov/ready/hyspilt4.html) to characterize dominant pathway of air masses during the wet season around the Banizoumbou site. Results clearly indicate that the monsoonal air mass coming from the Guinean Gulf, rich in sea salt aerosols, influences the site of Banizoumbou, and explain the "marine signature" in the collected precipitation samples. Except for the (Cl^-/Na^+) ratio, the other higher ratio values suggest a non-marine origin for the components, e.g., SO_4^{2-}, Ca^{2+}, K^+ and Mg^{2+}. These components are commonly attributed to the terrigeneous source. The marine contributions for Mg^{2+}, SO_4^{2-}, Ca^{2+} and K^+ are of 33%, 12%, 2% and 3% respectively.

Ca^{2+} was significantly correlated with total carbonates (r=0.84), Mg^{2+} (r=0.85) and SO_4^{2-} (r=0.83), at a confidence level higher than 1% (Table 2).This positive relationship confirms the importance of the particles coming from the desert and semiarid regions in the chemical composition of rainfall. The North African desert areas (Sahel and Sahara) are probably the most important mineral aerosol source (Kaufman et al., 2005). Due to the partial dissolution of soil dust terrigeneous components, rain in the Sahelian region is loaded with dissolved calcium and carbonates (calcite), which may account for the major part of the ionic concentrations of rain water. Calcium and carbonates ions are the most abundant in Banizoumbou rainwater, 27.3 and 28.2 μeq.l^{-1}, respectively. In addition to calcite, dolomite, gypsum and the dissolution of other key minerals such illite, smectite, palygorskite that compose African dusts explain the enrichment of Mg^{2+}, SO_4^{2-} and K^+ (Avila et al, 1997). This result is similar to that obtained in other regions of the world such as Asia

(Kulshrestha, 2005) or in the Mediterranean Basin (Löye-Pilot et al., 1986; Avila et al, 1997, 1998; Pulido-Villena, 2006) affected by air masses with high loadings in soil dust particles. Taking into account the marine contribution determined before, the terrigeneous contribution is as follows: 26.9 μeq.l^{-1} (98%) for Ca^{2+}, 8.3 μeq.l^{-1} (88%) for SO_4^{2-}, 7.3 μeq.l^{-1} (97%) for K^+ and 4.6 μeq.l^{-1} (67%) for Mg^{2+}.

The sum of the potential terrigeneous ions Ca^{2+}+Mg^{2+}+K^++SO_4^{2-}+HCO_3^- equals 75.2 μeq.l^{-1} and represents 52% of the total ionic content (about 144.1 μeq.l^{-1}) in the precipitation collected at Banizoumbou. Calcium and carbonates represent about 40% of the total ionic charge of precipitation. The terrigeneous contribution involves highest wet- deposition for Ca^{2+} (6.8 mmol.m^{-2}.yr^{-1}). Wet deposition of Na^+, Cl^-, Mg^{2+}, and SO_4^{2-} are: 4.3, 4.3, 1.7, and 2.3 mmol.m^{-2}.yr^{-1}, respectively (Table 5).

To compare with results obtained from other African sites, Table 5 gives annual VWM of terrigeneous and marine elements in selected IDAF sites representative of semi arid savannas and also present values along a transect from dry savannas to wet savanna to forest. The annual VWM concentrations of Ca^{2+} in Mali from 1997 to 2005 (Galy-Lacaux et al., 2009) and Niger (this work, 1994–2005) is very close and equal to 28.1 and 27.3 μeq.l^{-1} respectively. Lower values comprised between 12.0 and 18.7 μeq.l^{-1} are found for South African dry savannas (Mphepya et al., 2005). A significant result is the terrigeneous gradient found from the dry savanna to the forest with around 27–28 μeq.l^{-1} of calcium in dry savannas of Mali and Niger, 9.5 μeq.l^{-1} in the humid savanna of Lamto in Côte d'Ivoire (Yoboué et al., 2005) and with 8.9 μeq.l^{-1} in the forested ecosystem of Cameroon (Sigha et al., 2003). The annual VWM concentrations of sulfate present the same gradient from 7 to 9 μeq.l^{-1} in the dry savannas to 5.1 μeq.l^{-1} in the forest. Sulfate VWM in South African sites have higher concentrations, 10 times higher than in remote savannas sites of West Central Africa. Mphepya et al., (2005) have clearly demonstrated the anthropogenic influence on Amersfoort located in the Highveld and the recirculation of these polluted air masses affecting the Louis Trichardt site.

Calcium atmospheric deposition fluxes in Niger and in Mali are 6.8 mmol.m^{-2}.yr^{-1} and 10.8 mmol.m^{-2}.yr^{-1}. These fluxes represent calcium deposition near or in the source region of soil dust. Ca^{2+} wet deposition fluxes in African dry savannas of Mali and Niger, calculated with low annual rainfall depth (around 500 in Niger and 800 in Mali) are of the same order of magnitude or higher than total atmospheric calcium deposition (wet + dry) reported for the North of Europe (6.1 mmol.m^{-2}.yr^{-1}) (Hultberg and Ferm, 2004) or the Pacific coast of California (5.5 mmol.m^{-2}.yr^{-1}) (Schlesinger et al., 1982).

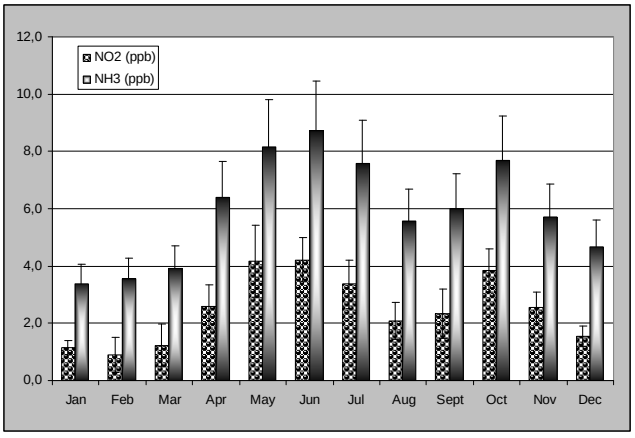


Fig. 2. Mean Monthly concentration of NH_3 and NO_2 in ppb at the Banizoumbou site from 1998 to 2004. Vertical bars represent the standard deviation around each monthly mean.

4.2 Nitrogen contribution

The annual VWM concentrations of NO_3^- and NH_4^+ concentrations are 11.6 and 18.1 μeq.l^{-1}, respectively, in precipitation at Banizoumbou (Table 5). They represent after carbonates and calcium concentrations the second highest contribution to the chemical composition of rain. This result confirms the importance of the nitrogenous signature in the semi arid savanna ecosystem. It confirms also data obtained in 1989 in Kollo, Niger (9.2 μeq.l^{-1} NO_3^- and 19.1 μeq.l^{-1} NH_4^+) (Modi et al., 1995) and in Banizoumbou in 1996 (12.3 μeq.l^{-1} NO_3^- and 12.9 μeq.l^{-1} NH_4^+ (Galy-Lacaux and Modi, 1998). At the scale of the African ecosystems, the amount of the inorganic nitrogen contained in the precipitation of dry-savanna site of Banizoumbou is comparable to those measured in the dry-savanna of Mali in Katibougou (NO_3^-=9.7, and NH_4^+=17.2 μeq.l^{-1}) (Table 5). South African semi-arid savannas of Louis Trichardt (LT) and Skukuza present VWM of Nitrate and Ammonium in the same order of magnitude (NO_3^-=8 to 8.1 and NH_4^+=9 to 9.7 μeq.l^{-1}) (Mphepya et al., 2005, 2006). Mphepya et al., in 2005 shows that the Amersfoort site (dry savanna near industrial sites) presents higher concentrations of nitrate (25.0 μeq.l^{-1}) and of ammonium (22.3 μeq.l^{-1}), in relation with industrial NO_x emissions.

Observing results along the transect dry-savanna/wet savanna/forest, annual VWM of ammonium in the wet savanna of Lamto is comparable to that in Banizoumbou (18 μeq.l^{-1}) (Table 5). Annual nitrate VWM is lower in the wet savanna and the forest ecosystems than in the dry savannas and is in comprised between 7 and 8 μeq.l^{-1}.

The NH_4^+ component of precipitation results of the incorporation of gaseous NH_3 and particles containing NH_4^+ in clouds and rainwater. Major sources of NH_3 included bacterial decomposition of urea in animal excreta and emissions

Table 5. Annual volume weighted mean concentrations in μeq.l^{-1} and wet deposition in mmol.m^{-2}.yr^{-1} (in parenthesis) for precipitation collected in selected IDAF sites.

Ecosystem	Location	Yearly rainfall*	Reference	pH	H^+	Na^+	K^+	NH_4^+	Ca^{2+}	Mg^{2+}	NO_3^-	Cl^-	SO_4^{2-}	$HCOO^-$	CH_3COO^-	$C_2O_4^{2-}$
Dry Savanna	Banizoumbou Niger	489.5 (1996)	Galy-Lacaux et Modi, 1998	5.67	2.1 (1.0)	7.7 (3.7)	4.7 (2.3)	12.9 (6.3)	31.2 (7.6)	5.6 (1.4)	12.3 (6.0)	7.4 (3.6)	8.6 (2.1)	4.5 (2.3)	2.7 (1.5)	
		495.1 (1994–2005)	This work	5.64	2.3 (1.1)	8.7 (4.3)	7.5 (3.7)	18.1 (9.0)	27.3 (6.8)	6.7 (1.7)	11.6 (5.7)	8.7 (4.3)	9.4 (2.3)	8.0 (4.0)	5.2 (2.6)	2.0 (0.5)
	Katibougou Mali	797.1 (1997–2005)	Galy-Lacaux et al. (2007) (pers. comm.)	5.44	3.7 (2.8)	6.3 (4.8)	3.7 (2.8)	17.4 (13.4)	28.1 (10.8)	4.5 (1.7)	9.7 (7.4)	6.6 (5.1)	7.1 (2.7)	10.8 (8.1)	5.5 (4.2)	2.4 (1.0)
Semi-arid	Amersfoort South Africa	755.0 (1986–1999)	J. M. Mphepya et al. (2005)	4.35	44.9 (33.9)	9.3 (7.0)	4.7 (3.5)	22.3 (16.8)	18.7 (7.1)	6.7 (2.5)	25.0 (18.9)	9.8 (7.4)	59.1 (22.3)	6.0 (4.5)	2.0 (1.5)	
Savanna	Louis Trichardt South Africa	748.0 (1986–1999)	J. M. Mphepya et al. (2005)	4.91	12.2 (9.1)	9.3 (7.0)	3.8 (2.8)	9.7 (7.3)	12.0 (4.5)	4.1 (1.5)	8.0 (6.0)	10.0 7.5)	14.5 (5.4)	11.5 (8.6)	4.3 (3.2)	
Wet Savanna	Lamto Côte d'Ivoire	1204.0 (1995–2002)	V. Yoboué et al. (2005)	5.16	6.9 (8.4)	6.3 (7.6)	2.4 (2.9)	17.6 (21.2)	9.5 (5.7)	2.7 (1.6)	7.7 (9.2)	7.1 (8.5)	6.5 (3.9)	11.1 (13.4)	6.0 (7.2)	1.4 (0.8)
Forest	Zoetele Cameroon	2029.0 (1996–2000)	Sigha et al. (2003)	4.92	12.0 (24.3)	4.0 (8.1)	5.0 (10.3)	10.5 (21.4)	8.9 (9.0)	2.4 (2.4)	6.9 (13.8)	4.3 (8.7)	5.1 (4.9)	8.2 (17.4)	3.2 (11.2)	1.0 (1.1)

*Yearly rainfall in mm, ( ): value of wet deposition.

from natural or fertilized soils (Schlesinger and Hartley, 1992), savanna fires and domestic fuel wood burning (Delmas et al., 1991; Brocard et al., 1996). In the Sahelian region, the main source of ammonia must be through hydrolysis of urea from animal urine in grazed areas (Galy-Lacaux and Modi, 1998). Also, in arid and semi arid regions with alkaline soils, ammonia emissions from soils is expected to be important (Schlesinger et al., 1992). Passive samplers measurements of NH_3 have been performed in Banizoumbou since 1998. Figure 2 shows the mean monthly variations of NH_3 concentrations calculated from the monthly mean over the seven measuring years (1998–2004). The ammonia source shows for all the year a similar pattern. First rains involve high nitrogenous compounds emissions both from the soils and after biomass burning emissions. The seasonality is well defined with two maxima, one in June at the beginning of the rainy season and one in October at the beginning of the dry season. The mean annual NH_3 concentration is 6 ppbv$\pm$2 ppbv. However, monthly variability on the period 1998–2004 and associated standard deviation are higher than the deviation on the annual mean. Carmichael et al. (2003) measured from September 1999 for one year ammonia concentrations in some selected sites in Africa, Asia and South America using passive samplers. Banizoumbou was part of this WMO/GAW pilot study and measured ammonia concentrations were higher than in India and South Asia. The high ammonium content of precipitation in Niger is clearly related to the intense source of ammonia attributed at the beginning of the wet season from soils emissions and animal excretion. The ammonium wet- deposition value equal to 9.0 mmol.m^{-2}.yr^{-1} for the 1994–2005 period at Banizoumbou. It is the highest deposition fluxes after calcium (Table 5). An annual VWM of ammonium of the same order of magnitude in the semi arid savanna of Mali-Katibougou and in the wet savanna of Lamto, is retrieved. For these ecosystems, the ammonium atmospheric deposition is also the highest compared to that from other compounds (13.4 and 21.2 mmol.m^{-2}.yr^{-1}).

The second nitrogenous contribution to rain chemical composition is nitrate. NO_3^- in rainfall is the final result of multiphase reaction processes of nitrogenous gases, atmospheric particles and cloud water. Nitric oxide (NO), in the non-burning season, is the major nitrogen compound released from savanna soils. Nitrogen compound flux necessary to equilibrate the Banizoumbou wet deposition of nitrate of 5.7 mmol.m^{-2}.yr^{-1} is about 2.6 ng (N) m^{-2} s^{-1}. NO emissions from savanna soils present high spatial and temporal variability linked to a large number of parameters (soil texture, soil water content, soil nitrogen status, burning, etc.) (Matson et al., 1990; Ambus and Christensen, 1994; Levine et al., 1996; Parsons et al., 1996). NO flux emission on infertile soils in semiarid savanna of South Africa of 3.5 ng N(NO) m^{-2} s^{-1} have been measured. According to Otter et al., in 2005, biogenic NO emissions from the south African savannas are equal to the amount of NO generated by biomass burning, but slightly less than those from industry. This result is in agreement with what was found in the Sahel. Original measurements of NO emission in the Sahelian savanna at Banizoumbou, where natural emissions are perturbed by grazing activities (Serça et al., 1997), showed rates of 6.09$\pm$2.64 ng N(NO) m^{-2}.s^{-1}. It indicates that savanna soils in Niger are strong emitters of NO. These measurements are also in agreement with surface NO_2 measurements performed at the Banizoumbou site (Fig. 2). The mean annual concentration of NO_2 is of 2.6 ppbv $\pm$0.4 ppbv. The seasonal pattern of NO_2 concentration shows clearly rain-induced nitric oxide emissions from semi arid savanna soils in the Sahelian region centered around the June maxima. Surface gaseous NO_2 concentration have been coupled to NO_2 columns from the Global ozone Monitoring Experiment (GOME) by Jaegle et al. (2004) to improve the NO_x emission budget over Africa during 2000. Regional NO_x emissions from savanna soils are therefore sufficient to equilibrate the wet deposition of nitrate measured at Banizoumbou.

The significant correlations between Mg^{2+} and NO_3^- and between Ca^{2+} and NO_3^-, both equal to 0.75, indicate potential heterogenous and multiphase chemical processes occurring between alkaline dust and gaseous nitric acid (Dentener et al., 1996; Galy-Lacaux et al., 2001). Also, the high correlation between nitrate and ammonium (r=0.74) demonstrates

that the nitrogenous components are associated in common processes. This is an indication of the availability of NH_4^+, formed after ammonia inclusion in rainwater**,** a second neutralizing agent in the precipitation. The influence of the terrigeneous and the nitrogenous contribution has been highlighted in the rain chemistry of the Sahelian region. Their role in chemical heterogenous processes and neutralizing effects in precipitation will be investigated and discussed in Section 5.

4.3 Acidic contribution

During the study period, precipitation pH in Banizoumbou ranged from 4.9 to 7.5. The mean VWM concentration of H^+ of 2.3 μeq.l^{-1} (Table 3) corresponds to a pH of 5.64. About 18% of the precipitation have a pH below 5.6, which is the pH of pure water in equilibrium with atmospheric CO_2. Most of precipitation events present pH higher than 5.6 and 1% is higher than 7.0. The median pH is close to 6.05. Galy-Lacaux and Modi have already shown that precipitation chemistry in the Sahelian region is strongly affected by alkaline species acting as buffering agents (Galy and Modi, 1998; Galy-Lacaux et al., 2001). This result has been widely emphasized in other part of the world affected by desert soil dust emissions that influence rain chemistry as for example in Spain or in the Mediterranean basin (Avila, 1997, 1998; Herut et al., 2000), in Asia (Kulshersthа et al., 2003, 2005; Hu et al., 2003). Acidity is neutralized by mineral dust, mainly carbonates, and/or dissolved gases (NH_3), before entering rain chemical content.

The sum of the potential organic and mineral acids (sulfur and nitrogen oxides) give a concentration of 34.6 μeq.l^{-1}. However, annual measured H^+ VWM is around 2.3 μeq.l^{-1} leading to a low deposition flux of 1.1 mmol.m^{-2}.yr^{-1}. Neutralization of rainwater in Banizoumbou can be evidenced by good correlations between major anions (NO_3^- and SO_4^{2-}) and major terrigeneous cations (Ca^{2+}, NH_4^+, Mg^{2+}) with the regression coefficient being 0.91. A similar regression has been studied between terrigeneous cations and organic acids r= 0.72. Ca^{2+} and NH_4^+ at Banizoumbou were the dominant neutralization substances.

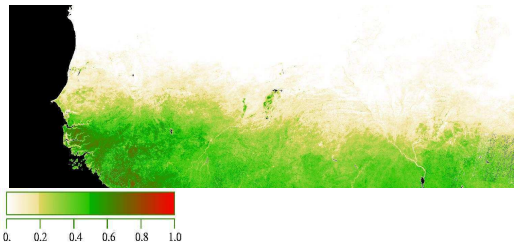
Table 5 shows a strong gradient of acidity along the African ecosystems: from the dry savanna, wet savanna to the forest, with pH from 5.64, 5.16, 4.92, respectively. Rain acidity in the dry-savannas sites of South Africa is higher (pH 4.35 in Amersfoort and 4.91 in Louis Trischardt). Mphepya et al. (2005, 2006) have shown that the two sites are affected by NO_x and SO_x industrial emissions of the highveld (Turner et al., 1996).

The acidity in Banizoumbou is weakly correlated to mineral acidity (H^+/NO_3^- r=0.46 and H^+/SO_4^{2-} r=0.31). Correlation with to organic acids like formate (r=0.81) and acetate (r=0.57) is higher. The high measured level of organic acidity represent a new result. In 1996 precipitation study, Galy and Modi (1998) have mentioned the original signature of organic acidity (formate VWM of 5 μeq.l^{-1} and acetate VWM of 4 μeq.l^{-1}). In this study, the annual VWM of formate is 8 μeq.l^{-1}, 5.2 μeq.l^{-1} for acetate and 2.0 μeq.l^{-1} for oxalate. This result is comparable to results observed in almost all the dry savannas.

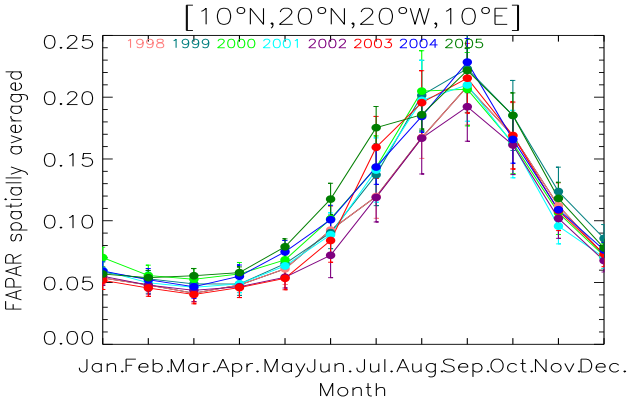
The atmospheric sources of organic acids in rain have not yet been properly identified. Some proposed sources include vegetation emissions (Guenther et al., 2006) and in-cloud process (specially for formic acid) such as the hydrolysis of aldehydes followed by aqueous phase reactions with OH radicals (Chameides and Davis, 1983; Graedel and Crutzen, 1993), soil (Sanhueza and Andreae, 1991), emissions from biomass burning (Talbot et al., 1988, 1990) and also oxidation from precursor compounds in the gas phase.

Galy-Lacaux and Modi (1998) have mainly attributed the organic acidity contribution in precipitation composition to the vegetation source of Volatile Organic Carbon. Keene and Galloway (1986) have demonstrated that active plan growth periods are direct or secondary major source of organic acids in precipitation in continental regions. In the Sahel, the response of vegetation to the first rain pulse is very active. There is a lag-time between these first rains and the first vegetation cover (Jarlan et al., 2005; Martiny et al., 2005). A long time series of space remote sensing products has been developed to estimate the FAPAR for various optical instruments (Gobron et al., 2000, 2006, 2007, http://fapar.jrc.ec.europa.eu/). This biophysical indicator has been chosen because it reveals the level of vegetation photosynthetic activity, which signifies the amount, state and health of vegetation canopies. This value is derived from the closure of the energy balance equation inside the canopy and corresponds to the normalized radiant flux in the Photosynthetic Active Radiation (PAR) region of the solar domain. Figure 3 presents the time series of FAPAR that covers January 1998 to December 2005 over the geographical region representing the Sahel defined by [10° N, 20° N, 20° W, 10° E]. Figure 3a displays the FAPAR value using a color scale varying from white, green to red for the value of FAPAR about 0, 0.5 to 1.0 over the Sahel for October 1998. It gives an example of the maximum of observed vegetation. In Fig. 3b FAPAR monthly time-series are displayed after spatial averaging over the Sahelian region. Different colors are for the different years. The strong seasonal cycle is clearly visible and the yearly average variability for the Sahelian region is smaller. This seasonal cycle with a rapid growth of vegetation beginning in May–June reaches a maximum in September. It is hypothesized that the organic acidity measured in Banizoumbou precipitation is related to the vegetation cycle in the Sahel. This vegetation is certainly VOC emitters but no measurements are available to obtain an order of magnitude from this source.

Moreover, in the Sahelian region, the biomass burning source could explain a significant part of the organic acidity retrieved in precipitation. For the first time, we measured the oxalate concentrations in precipitation (VWM of



(3a) FAPAR in October 1998.



(3b) FAPAR profiles.

Fig. 3. **(a)** Map of FAPAR for the Sahel region in October 1998. **(b)** Time series of spatially monthly averaged *F*raction of *A*bsorbed *P*hotosynthetically *A*ctive *R*adiation (FAPAR) values derived over the Sahel region from 1998 to 2005. The vertical bars indicate the standard deviation, thus indicating the current spatial variability over this geographical window.

2 μeq.l^{-1}) that is an indicator of the biomass burning source (Baudet et al, 1990). A significant correlation measured between K^+ and oxalate (r=0.72) and ammonium (r=0.63) confirms this result. To investigate the potential influence of the biomass burning source in the Sahelian region, historical emissions of biomass burning for the years 1997–2003 obtained from Granier et al. (2007), are analyzed. A tracer of combustion (Black Carbon=BC) have been monthly averaged on the geographical window defined by [10° N, 20° N, 20° W, 10° E]. This inventory crosses the satellite burnt areas data of the year 2000 (from Global Burnt area 2000 product; Tansey et al., 2004) and satellite active fire pixels data of the years 1997–2003 (from World Fire Atlas /ATSR product; see Arino and Rosaz, 1999). Monthly and annual BC emissions are calculated following the methodology described in Konaré et al. (2007) (Fig. 4). Results emphasize the presence of biomass burning in the "Sahelian window" with a defined seasonal cycle. Dry season takes place from October November to April and the wet season from May to October. BC emissions are non negligible in May and June with emissions from 0.6 to 4 Gg of BC. To compare, the maximum is measured in January with a mean BC emission of 17 Gg over the period 1997–2003.

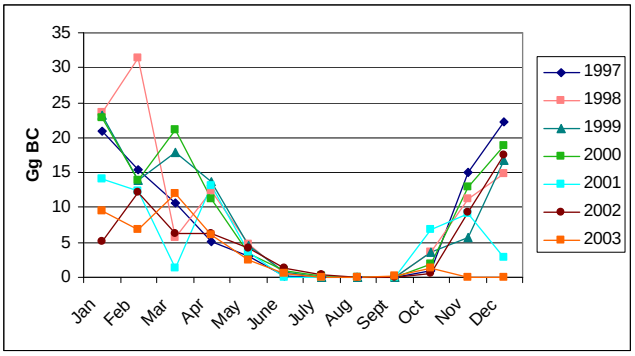


Fig. 4. Monthly Black Carbon (BC) emission in Gg C, as tracer of the biomass burning in the Sahel region defined by [10° N, 20° N, 20° W, 10° E] from 1997 to 2003.

We conclude that in the Sahelian region, biogenic emissions from vegetation are active at the beginning and in the heart of the wet season and biomass burning sources at the end of the wet season. The combination of these two sources could explain the organic acidity content of the precipitation.

5 Inter-annual variability and trends of rain chemistry in Banizoumbou

VWM concentrations for each element and each year (1994–2005) are given in Table 3. Annual VWM concentration and wet deposition fluxes are displayed on Fig. 5a and b. The annual ionic charge is defined as the sum of the VWM for one year. The mean ionic charge in precipitation (1994–2005) is represented on Fig. 5a as a dash line and is equal to 144.1 μeq.l^{-1}. Over the period 1994–2005, the charge varies from a minimum of 111.9 μeq.l^{-1} in 1999 to a maximum of 158.5 μeq.l^{-1} in 2001. The fluctuation of the ionic charge in precipitation on the eleven year period is about ±10%, except for 1999 (−22%).

The mean pH is not highly fluctuating from year to year with a maximum deviation of ±0.1. It has been also noticed that from one year to the next one, the dominant ions are the same at Banizoumbou. The inter-annual variations around the mean (1994–2005), calculated for groups of elements representative of the different source identified previously (Sect. 4), are analyzed. The Na^+, Cl^- and $ssMg^{2+}$ VWM range from 6.2 to 12.6 μeq.l^{-1}, from 5.4 to 12.2 μeq.l^{-1} and from 1.4 to 2.9 μeq.l^{-1}, respectively. These co-fluctuations have the same pattern. The mean variation for the marine source is ±5% with a maximum deviation ±20%. Mean deviation for the terrigeneous contribution including $nssCa^{2+}$, $nssMg^{2+}$ and $nssSO_4^{2-}$ is ±3%. Variation for nss K+ is around ±9%. Maximum deviations around the annual VWM for the terrigenous contribution are comprised between ±15% and ±20%. Concerning the nitrogenous group formed by NH_4^+ and NO_3^- and the organic component with

Table 6. Estimation of the marine, the nitrogenous, the organic, the acidity and the terrigenous contribution to the rain chemical content along a transect of African ecosystem.

	Dry savanna Banizoumbou (1994–2005) This work.	Wet savanna Lamto (1995–2002) V. Yoboué et al. (2005)	Forest Zoétélé (1996–2000) Sigha et al. (2003)
Marine $Na^+ + Cl^-$	12%	13%	10%
Nitrogenous $NH_4^+ + NO_3^-$	21%	25%	21%
Organic $HCOO^- + CH_3COO^- + C_2H_5COO^-$	9%	17%	14%
Terrigenous $Ca^{2+} + Mg^{2+} + SO_4^{2+} + K^+ +$ tcarbonates	55%	36%	38%
Acidity H^+	2%	15%	7%

formate and acetate, the same result is observed. Variations around the mean for the nitrogenous and the organic contribution part are maximum and equal to ±5%. However, the yearly deviations for formate and acetate present a higher variability with maximum fluctuations equal to ±20% and ±30%, respectively.

The total ionic content of the precipitation is function of the amplitude of the main sources of atmospheric gases and particles and the rainfall regime and the associated annual total rainfall at the studied site. The analysis of interannual variability reflects clearly the potential variation of the intensity of atmospheric sources associated to a second important factor, i.e the variation of the annual rainwater depth. The amount of water determines the scavenging of the different atmospheric chemical compound and directly acts as a dilution factor. The analysis of rainfall in the Sahel shows a strong spatial and temporal variability of the same order of magnitude that we found for chemical composition of precipitation (Balme et al., 2006). Another important result is the discrete aspect of the Sahelian rainfall. This process directly affects rain chemistry content and wet deposition fluxes of nutrients. The weight of each process is somewhat difficult to estimate.

The mean Wet Deposition calculated for all the database is 60.1 mmol.m^{-2}.yr^{-1} (Fig. 5b). The fluctuation of the wet deposition in the dry savanna of Banizoumbou for the period (1994–2005) is ±25%. Around this mean value, the WD varies from a minimum of 44.4mmol.m^{-2}.yr^{-1} in 2000 to a maximum of 81.0 mmol.m^{-2}.yr^{-1} in 1998 (+35%). These two extreme values correspond to extreme years with positive rainfall anomalies in 1998 and with negative rainfall anomalies in 2000. Wet deposition fluxes are directly correlated to both the annual rainfall amount and the chemical content measured in precipitation. At the Banizoumbou site it has been possible to determine the mean annual chemical characteristics of precipitation for the 11 years under study. Thus, it can be said that wet deposition is mainly influenced by the annual total rainfall. One can observe that the two rainiest years 1994 and 1998 suffer the higher annual wet deposition. The input of nutrients to the ecosystems removed by wet deposition can be perturbed and diminished if severe drought in arid- and semi-arid ecosystems persist as in the Sahel.

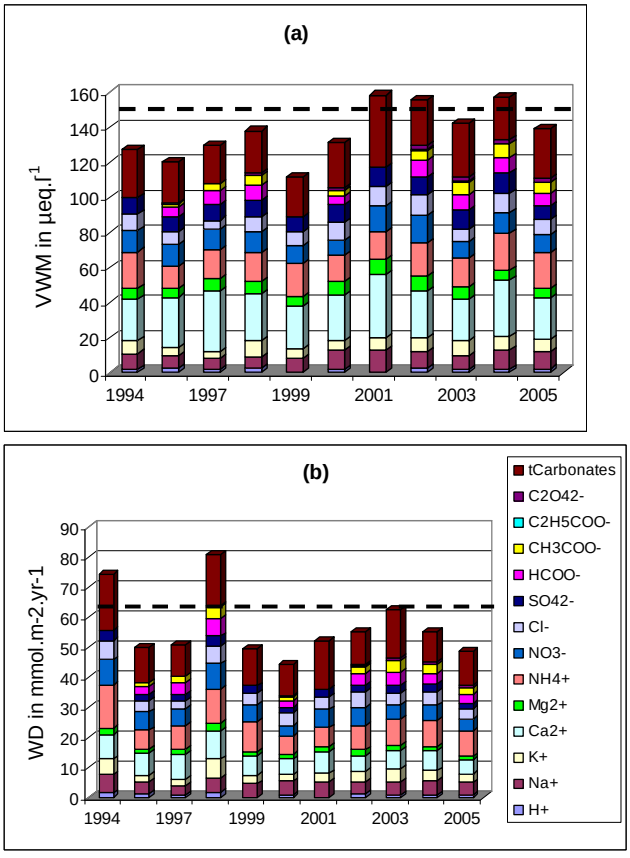


Fig. 5. (a) Annual Volume Weighted Mean concentration (μeql^{-1}) in precipitation over the eleven years period (1994–2005) at the dry savanna site of Banizoumbou. **(b)** Annual Wet Deposition fluxes (mmol.m^{-2}yr^{-1}). The horizontal bars indicate the mean VWM and WD calculated from all the database.

To compare our long term measurements study in Niger (natural dry-savanna), we see that in developed countries such as Central and Western Europe (Puxbaum et al., 2002), in North America (Likens et al., 2001), in Central Austria (Puxbaum et al., 2002) and in Brazil (Fornaro et al., 2006), long-term precipitation chemistry trends are mainly controlled by reduction on the sulfur and nitrate-nitrogen emissions. The main result of these long-term studies shows

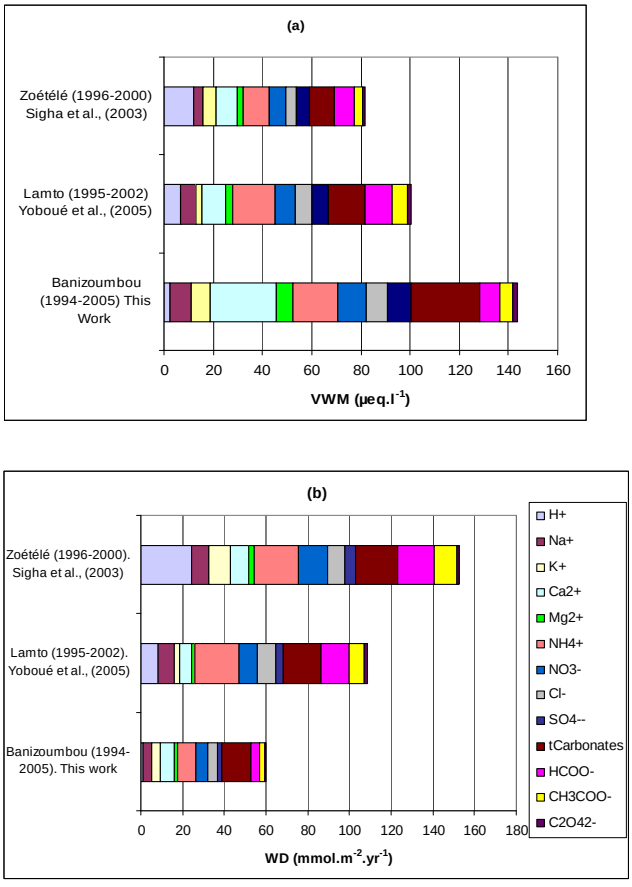


Fig. 6. (a) Annual Volume Weighted Mean concentration (μeq.l^{-1}) representative of the African ecosystems: dry savanna-wet savanna-forest. **(b)** Annual wet deposition fluxes for the ecosystem transect (mmol.m^{-2}yr^{-1}).

a decrease of the free acidity reflecting a gradual decrease of atmospheric SO_2 concentrations according to sulfate reduction decisions. The deposition loads, thus present a trend dependant on emission strength.

This study over the Sahelian region is unique for its long-term monitoring of rainfall chemistry. Results are different from those found in developed countries. The inter annual variability of the annual rainfall VWM concentrations shows that the source input over the period 1994–2005 present a natural variability from one year to the next. The observed variability around $\pm$25% is of the same order of magnitude than the rainfall regime variability measured in the Sahelian region. As such, rainfall chemistry content appears to be strongly influenced by the intensity (liquid water content) and the temporal repartition of rainy events. On the other hand, wet deposition, influenced by the atmospheric charge in chemical compounds and the annual total rainwater is more variable. In the Sahelian region, it presents a trend directly driven by the annual rainfall.

6 Comparison of rainwater chemistry in Niger to other sites: focus on the transect dry savanna-wet savanna and forest in West/Central Africa.

In the IDAF framework, long-term measurements of precipitation chemistry characteristics for two great West/Central African ecosystems have been recently established. The site of Zoétélé in the equatorial forest of Cameroon has been studied from 1998 to 2000 and the humid savanna of Lamto in Côte d'Ivoire from 1996 to 2002 (Sigha et al., 2003; Yoboué et al., 2005). Results for the ecosystems transect: i.e., dry savanna-wet savanna and forest are displayed in Fig. 6a and b. The first result is to compare the total chemical charge of the precipitation (FIg. 6a). A strong gradient from 143.7, 100.2 and 86.6 μeq.l^{-1} at Banizoumbou, Lamto and Zoétélé, is observed respectively. To study the chemical composition of rain along the transect, we group the different ionic species for each site according their characteristics of atmospheric sources identified in the mean rainfall composition (Table 6).

The marine contribution mainly represented by sodium and chloride is comparable in the dry savanna of Niger and the wet savanna of Côte d'Ivoire, even if Lamto is located at 120 km of the coast and Banizoumbou to about 1000 km. For Zoétélé in Cameroon, relatively close to the coast (200 km), the marine contribution is very low and has been attributed to a discharge in marine elements caused by orographic rains for air masses coming from the ocean. Generally, in all the African ecosystems, the marine contribution is low and estimated to represent 10% to 13% of the rain chemistry. We have discussed in Sect. 4 the high contribution of the nitrogenous compounds in all the ecosystems, higher in the dry-savanna than in wet-savanna and forests. This result is confirmed by measurements performed in Mali (Table 5). The contribution to the total chemical content of rain is however estimated to be quite comparable in all the ecosystems and equal to 21% to 25% of the total. The third chemical component identified in the rain is the organic component. Indeed, the organic component has been found as important in the dry savanna than in the other ecosystems. This result is new and can be somewhat surprising. It is thought that vegetation and soils plays an important role in semi arid and arid ecosystems with a seasonal cycle well marked (sparse measurements exist on natural emissions from these ecosystems). The dry savanna is certainly less impacted by the biomass burning source and it explains a lower contribution in organic acidity with 9%, compared to the wet savanna and the forest with 17% and 14% respectively. When the H^+ contribution is analyzed, a strong positive gradient from the dry savanna to the forest is found. The free acidity attributed to H+ represent 15% of the total chemical composition of the rain in the forested ecosystem. Similar results are obtained in the Amazonian forested ecosystems (Williams et al., 1997; Lara et al., 2001). On the African continent, this study along the transect shows that the potential

acidity coming from the nitrogen oxides is equivalent on all the ecosystems. The organic acidity has a gradient from the dry-savanna to the forest, but a higher contribution from the wet-savanna compared to the forest is noticed. The strongest contribution observed along the transect concern the terrigeneous contribution. The main ion is calcium with concentrations varying from 27.3 μeq.l^{-1} in dry savanna, to 9.5 in wet savanna and 8.9 μeq.l^{-1} in forest. It exists a negative gradient of the major terrigenous species concentrations along the transect dry savanna-wet savanna-forest from north to south of West Africa in relation with source region of dust and their potential transport. This gradient affects the acidity of precipitation along the transect of ecosystems by governing the concentrations of potential neutralizing agents.

To explain the acidity gradient, it is important to analyze key processes in charge of the neutralization of the free acidity. Recent studies in heterogeneous chemistry processes represented by the potential interactions between gases, water and particles have been published: i.e., in the Pacific (Prospero et al., 1995), for the wet-savanna of Africa (Yoboué et al., 2005, for Asian aerosol (Carmichaël et al., 1996, 1997), or in India (Kulshrestha, 2003, 2005). In Africa, an original study in the Sahelian region has been conducted through IDAF field measurements and SCAPE modeling simulations (Galy and Modi, 1998; Galy et al., 2001, 2003). Considering the importance of heterogeneous process in the tropical chemistry, it has been decided to recalculate from the measurements made at Banizoumbou over the period 1994–2005, the estimation of the gaseous and particle phase contribution to the chemical content of the precipitation. To investigate the relative contribution of particles and gases in rainwater, Yoboué and al. (2005), have proposed a calculation of PCrain for the relative particle contribution and GCrain for the gaseous one. The non-volatile cations Ca^{2+}, Na^{+}, Mg^{2+} and K^{+} are considered as representative of the mineral particle phase. In order to apply the neutrality principle, the sum of the cations is equilibrated into an equivalent sum of anions. At the Banizoumbou site, the mean relative contribution in rainwater is 70% fro particles and 30% for gases (1994–2005). Using the same concept, identical computation was made for the two other ecosystems using mean characteristics presented in Table 5. For the wet savanna of Lamto, we obtain a particulate contribution of 42% and a gaseous contribution of 58% for gases, and in the forest of Zoétélé 50% for particulate phase and 50% for the gas phase.

In Fig. 6b the wet deposition fluxes of each species along the transect of ecosystems are displayed. A clear negative gradient of the global load in precipitation from the dry savanna to the forest (VWM in μeq.l^{-1}) is identified (Fig. 6a). To the opposite, the wet deposition fluxes is driven by the strong rainfall gradient along the ecosystems transect: with 495.1 mm in the dry savanna of Banizoumbou (Niger), 1204 mm in the wet savanna of Lamto (Côte d'Ivoire) and 2029 mm in the forested ecosystem of Zoétélé (Cameroon). Thus, the wet deposition fluxes is more than two times higher in the forest than in the dry savanna. The total mean annual wet deposition is estimated to be equal to 60.0 mmol.m^{-2}.yr^{-1} in Banizoumbou, 108.6 mmol.m^{-2}.yr^{-1} in Lamto, and 162.9 mmol.m^{-2}.yr^{-1} in Zoétélé.

7 Conclusion

Within the framework of the IDAF monitoring network, long-term measurements and analyses of precipitation chemistry carried-out in a rural area of the Sahelian region from 1994 to 2005. Rainwater chemistry in Banizoumbou, a representative site for the African semi-arid savanna ecosystem, was controlled by soil dust emissions associated to a high terrigeneous contribution. Calcium and carbonates have the higher VWM concentrations and represent about 40% of the total ionic charge of precipitation. The other signatures of atmospheric sources in the Sahelian precipitation are highlighted by the relatively high nitrogen (ammonium and nitrate) and organic ion contents (formic and acetic acids) in precipitation. The nitrogen component is the signature of strong ammonia sources related to animals excreta and strong NO_x emissions from savannas soils rain-induced at the beginning of the wet season. The mean annual NH_3 and NO_2 concentration measured in Banizoumbou (6 ppbv and 2.6 ppbv) and their well marked seasonal cycle confirm this result. Biomass burning and photochemical oxidation of biogenic precursors from vegetation have been identified as potential processes contribution to the formation of organic acids in Sahelian precipitation. The organic signature in the dry-savanna of Banizoumbou is comparable to the measured level in the wet savanna or in the forest. The monsoon airmass coming from the Guinean gulf, rich in sea salt aerosols, influence the site of Banizoumbou, and explain the marine signature in the collected precipitation samples. We measured a low acidity in precipitation (pH=6.05). Precipitations present a high buffering capacity with high VWM concentration of NH_4^+ and Ca^{2+}. The interannual variability of the rainwater chemical composition presents fluctuations between $\pm$5% and $\pm$30% mainly attributed to the variations of sources strength, and to the variations of the annual rainfall depth and its temporal distribution. The wet deposition flux in the Sahelian region fluctuates around $\pm$25% from 1994 to 2005. The study of the African ecosystems transect: dry-savanna-wet savanna-forest indicates a strong negative gradient of the total chemical load of precipitation related to the the terrigeneous contribution gradient. The wet deposition fluxes present an inverse result linked to the strong rainfall gradient along the ecosystems transect.

In the future, it seems necessary to study the chemical composition of the wet deposition in association with the distribution of precipitation to try to understand for example how the numbers of convective systems or rain efficient convective systems affect the wet deposition chemistry.

Spatio-temporal distribution and intermittency of rainfall in the Sahel are key elements to understand hydrological impacts but also wet deposition chemistry in semi-arid regions. Moreover, further studies on sources intensity and dynamic transport of atmospheric compounds transport are needed to understand the interannual variability of rain chemistry and wet deposition. To integrate all these processes, it is planned to compare and integrate the experimental results presented here into a modelling study using the ORISAM-RAD-TM4 global model (Guillaume et al., 2007). ORISAM-RAD-TM4 model include a detailed 6-bin dynamic sectional aerosol module. This module will allow to take into account the heterogenous chemistry, key process identified in the control of the rain acidity and associated wet deposition in the Sahelian region. Multi-year simulation will be driven in order to scrutinize the interannual variabilities of wet deposition chemistry over Africa using updated emissions inventories (Granier et al., 2007; Guenther et al, 2006).

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